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Sensor-less adaptive fuel concentration control for direct methanol fuel cells under varying load

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HIGHLIGHTS

► We propose a sensor-less algorithm to maintain methanol consistency.
► Varying load poses a problem to maintain consistent concentration.
► We consider steady and transient behaviors caused by varying load.
► This method avoids complex derivations while maintaining fast response.

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ABSTRACT

This study proposes a sensor-less adaptive fuel concentration control (SAFCC) algorithm to maintain methanol concentration consistency for direct methanol fuel cells (DMFC). Methanol concentration has a dominant effect on fuel cell performance, however varying load poses a problem to maintain consistent concentration. The transient response for varying load is influenced by a series of interactively complex factors. Here, we introduce the SAFCC algorithm by measuring the present voltage and checking the decrease from a reference voltage. Compared to existing literature on sensor-less control methods, the delicate but simple algorithm can avoid complex mathematical derivation while maintaining quick decision to inject fuel. This algorithm can be used under both of steady and dynamic loading conditions and has the adaptive capability suitable for degraded fuel cells. Practical experiments for several scenarios are carried out with satisfactory results.

1. Introduction

Energy shortage has become a serious problem in recent years. Many kinds of renewable energy are taken into consideration as alternatives. Among these, hydrogen energy is one of the most ideal candidates. Fuel cells is a device which transforms hydrogen energy into electricity. The direct methanol fuel cell (DMFC) is a promising power source for low power applications such as portable electronics [1]. However, many challenges exist, such as methanol crossover, management of heat and water, slow reaction kinetics, durability etc. [2]. Many research topics focus on catalytic materials, membrane, and surface characteristic analysis of flow channel for DMFC [3–5]. These research directions generally discuss chemical reactions and internal structure of DMFC. For applications on portable devices, the volume, power generation efficiency, and cost must be considered. Especially methanol concentration influences the performance significantly: Both low and high concentrations decrease the efficiency of energy transformation. The methanol crossover effect caused by high methanol concentration wastes fuel and reduces cell voltage [6]. Meanwhile low methanol concentration yields lower power output. Therefore, it is necessary to keep methanol concentration yields in an adequate range.

Sensors can directly measure the methanol concentration of the DMFC. Xie et al. [7] used a sensor connected to the methanol pump to monitor and control the methanol concentration. Methanol concentration sensors are generally classified into two groups: electrochemical and physical [8]. Sung et al. [9] established regression models based on measurements of sound propagation speed against methanol concentration where the real-time concentration can be determined from measured speed of sound. Geng et al. [10] developed an electrochemical methanol concentration sensor using an alternating pulse working voltage. The sensor shows high sensitivity to methanol with a good linearity

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over a certain concentration range. Although sensors measure concentration directly, the disadvantages are high cost and the increase of physical size especially for applications in portable devices.

Accordingly, how to maintain optimal state of methanol concentration without sensors has become an important issue for DMFCs. Among not many articles in the literature, the works [11–14] used the equations related to methanol consumption to estimate the methanol concentration. Chiu and Lien [11] proposed a three-dimensional measurement space and constant concentration surfaces and used cell voltage to develop an algorithm of estimating fuel concentration in a liquid-feed system. However, this method has no adaptive capabilities and problem may arise since the voltage decreases with system decay even under the same methanol concentration. Shen et al. [12], according to Chiu and Lien's algorithm, improved real-time controlling methanol and total quantity of fuel, such that the membrane electrode assembly voltage decays coefficients are pre-established. Ha et al. [13] built a sensor-less control logic based on the estimation of the rates of methanol consumption and constructed a database of the rates of methanol consumption under various operating conditions. Arisetty et al. [14] performed the development of an *in situ* methodology which uses the measured cell voltage as feedback to regulate the methanol feed concentration for maximum power density, where the fuel loss as a function of methanol concentration is evaluated by oxidizing the crossover methanol at the cathode exhaust and measuring the CO_2 mass flux. Other sensors-less control methods only observes the output state. The researches [15–18] apply cell-operating characteristic to regulate the fuel concentration. Chang et al. [15] proposed an impulse response based on discrete time fuel injection (IR-DTFI) control scheme. Chen et al. [16] applied the IR-DTFI control scheme for developing a 20 W DMFC power source for portable devices which are suitable for steady load. Chang et al. [17] proposed a modification of IR-DTFI for DMFC operating under dynamic loading conditions. Then, Chang et al. [18] developed a current integral technique to calculate the quantity of fuel required at each monitoring cycle, and called it modified impulse response based on current integral and discrete time fuel injection (IR-CIDTFI) control scheme. However, the equation calculating is easily leading to cumulative error.

Our method is much like the works [15–18], which are easy and fast to implement. According to the voltage response under step changing load, we find an interesting characteristic whereby the status of sufficient or insufficient concentration can be identified. Then, we propose a new judging process to evaluate performance degradation and can determine the right time of injecting fuel. This judging process can achieve faster response with the simple control algorithm. In addition, the adaptive capability of accommodating degraded cells is verified by experiments in this work. In light of the above, the advantages of our method are with no cumulative error, fast response, simpler control frame and adaptive capability.

The rest of the paper is organized as follows. The behaviors of DMFC under both of sufficient and insufficient concentration conditions are explained in Section 2. The design guidelines and scheme of the proposed algorithm are illustrated in Section 3 and shown to solve the problem of dynamic load conditions and system decay. Some experiments are carried out to verify the capacity of different situations, and the results are shown in Section 4. The final section is the conclusion.

2. Behaviors of DMFC

The DMFC is a specific type of proton exchange membrane fuel cells. The methanol electro-oxidation reaction in acidic electrolytes for DMFC is [4]:

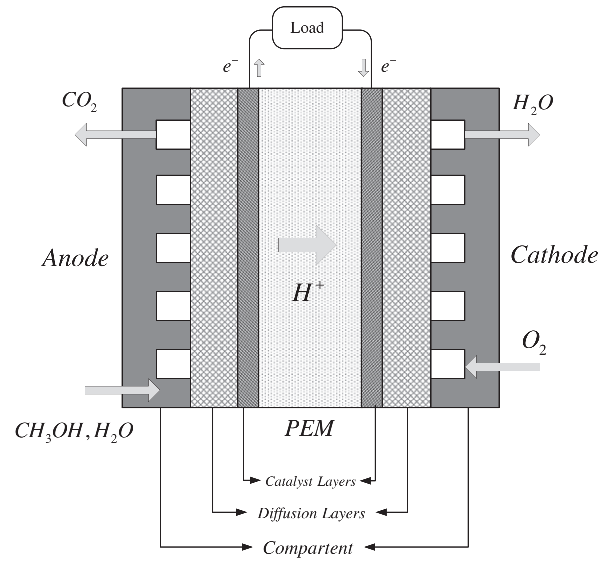

Fig. 1. The operating principle of DMFC.

$$\text{Anode}: CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

$$\text{Cathode}: \frac{2}{3}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$$

$$\text{Overall}: CH_3OH + \frac{2}{3}O_2 \rightarrow CO_2 + 2H_2O$$

The methanol concentration directly affects the output performance. Hence, maintaining the optimal methanol concentration is important. Fuel cells running on methanol require water as a reactant at the anode, which produces CO_2 at the anode as a waste product. Fig. 1 illustrates the operating principle of direct methanol fuel cell (DMFC). The fuel cell voltage

$$V = E_{\text{thermo}} - V_{\text{act}} - V_{\text{ohm}} - V_{\text{con}}, \quad (1)$$

where E_{thermo} is the cell thermodynamic potential drop; V_{act} is the activation overpotential; V_{ohm} is the ohmic overpotential; and V_{con} is the concentration overpotential [19]. From the relationship in (1), the output voltage of a real fuel cell is less than thermodynamically predicted voltage output due to irreversible losses. Fig. 2 shows the polarization curve of fuel cell [20]. In addition, the more current

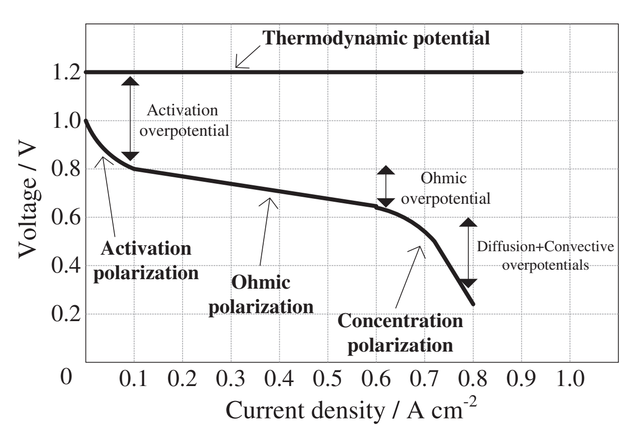

Fig. 2. Polarization curve of fuel cell.

Table 1
Factors affecting the transient state.

Main categories	Detailed factors
Electrochemical response characteristics	Electrochemical response of the anode and cathode reactions Charging characteristic at the interfaces between the electrode, electrolyte and solid polymer membrane Products of carbon dioxide and its release from the anode catalyst layer
Mass transfer characteristics	Method to the catalyst sites through the diffusion layer and catalyst region Methanol through the membrane Oxygen to the cathode Transport of water at the cathode catalyst layers
Physical characteristics	Methanol solution and carbon dioxide gas through the anode diffusion layers Hydrodynamic methanol solution and carbon dioxide gas in the flow bed Heat release and temperature response of the cell

that is drawn from the cell, the greater the losses. There are three major types of fuel cell losses, which give a fuel cell *I*—*V* curve its characteristic shape.

The first type is the activation losses due to electrochemical reaction. The second type is the ohmic losses due to ionic and electronic conduction. The final type is the concentration losses due to mass transport. Equation (1) represents the steady-state voltage correctly. However, there is no ideal and simple representation for transient behaviors until now, because the dynamic response of the DMFC is affected by a series of complex interactions [21,22]. The overall dynamic response of the DMFC depends on several interactive factors, which can be classified into three main categories such as chemical response characteristics, mass transfer characteristics, and physical characteristics of fuel and product. The first category is related to the electrochemical reaction which includes reactions of anode and cathode sides, charging characteristic, and increase of chemical products. The second category is related with the mass transfer characteristics which includes methanol through different regions and oxide and water through different layers at cathode. The third category is related with the physical characteristics which includes methanol state transform between the liquid and gas phases and carbon dioxide gas in different layers at the anode. Table 1 shows the detailed factors affecting the transient state.

In addition, the output voltage changes with the varying loading current. In previous literature, many experiments have explored the transient response characteristics. Two apparent transient phenomena, overshoot and undershoot, occur when the loading current changes [23,24]. We will give a deep observation for the output transient behaviors in the following.

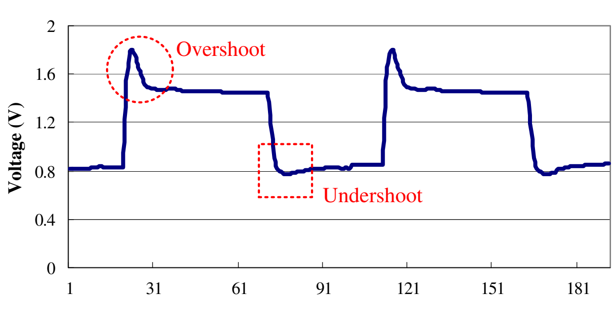

Fig. 3. Transient phenomena under sufficient concentration condition.

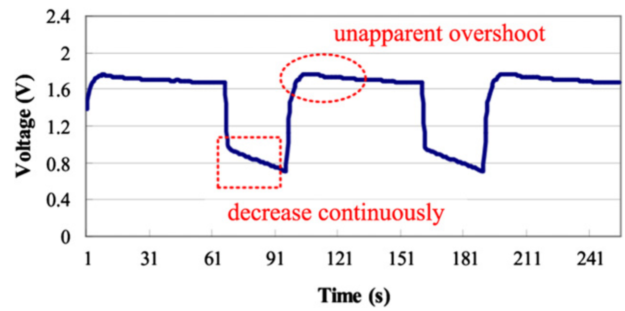

Fig. 4. Transient phenomena under insufficient concentration condition.

2.1. Output behaviors under sufficient methanol concentration

We first consider the response under sufficient concentration condition. Under constant load, the output voltage will be at a constant level called the nominal value. When DMFC operates under step changing load, the transient response occurs. The circled area and squared area shown in Fig. 3 are accordingly the typical patterns for the overshoot and undershoot phenomena under sufficient concentration condition. When the loading current changes from high to low, the output voltage will change from low to high and overshoot occurs. For the overshoot phenomenon, the output voltage exceeds over and then returns back to the steady-state nominal value. On the other hand, when the loading current changes from low to high, the output voltage will change from high to low and undershoot occurs. For the undershoot phenomenon, the output voltage falls below and then returns back to the steady-state nominal value.

2.2. Output behaviors under insufficient methanol concentration

The output voltage response under insufficient methanol concentration exhibits different phenomena. Fig. 4 shows the transient response of DMFC under insufficient concentration condition.

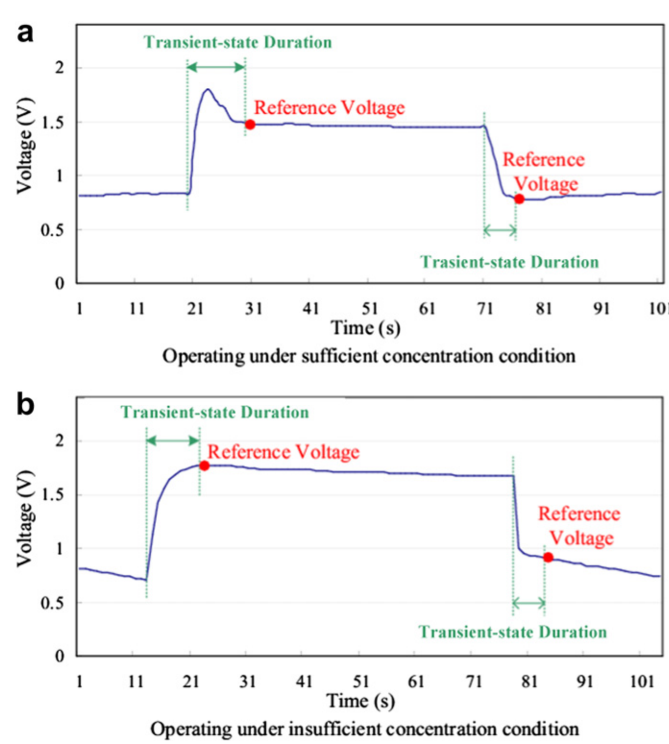

Fig. 5. The settings for transient-state duration and reference voltage.

Both the overshoot and undershoot phenomena under step changing load are no longer apparent. Especially, the output voltage in the squared area is less than the nominal level. It decreases continuously and cannot return back to the steady-state nominal value.

3. Building a control algorithm for DMFCs

3.1. Design guidelines

We design an SAFCC algorithm from observing cell output state, where the control approach is supposed to meet the following criteria:

- Continuous monitoring: It must continuously monitor the methanol in order to achieve the capacity of fast response to prevent from staying too long in the state of unsuitable concentration.
- Adaptiveness: It has the capacity to work with various DMFC modules with different states of decay. In other words, the control algorithm is independent of the status for DMFC's parameters.
- Dynamic operation: It works for both constant load and step changing load conditions.

As shown in Fig. 3, the transient response takes an amount of time to return back to steady-state in the sufficient concentration condition. These durations can be approximately determined by experimental experiences. The overshoot and undershoot durations are typically less than 10 s and 5 s, respectively. After the transient time, we set the first measured time and its voltage value as the reference point and the reference value, respectively. These settings are shown in Fig. 5. Under the sufficient concentration condition, the output voltage does not further decrease after the reference point and is kept in a fixed value after the transient time. This in turn means that the voltage is maintained around the reference voltage. On the other hand, for insufficient concentration the output voltage continuously decreases after the reference point. In other words, the output voltage falls off the reference voltage after the transient time due to low methanol concentration.

In light of the above, the responses under concentration-sufficient and concentration-insufficient conditions are very different. Based on this observation, we can design an SAFCC algorithm to maintain the methanol concentration in a suitable range. We describe the detailed algorithm in Section 3.2.

3.2. SAFCC algorithm

Fig. 6 shows the flow chart of the SAFCC algorithm. The control algorithm starts from Step A1. Step A2 determines the reference voltage value which is the first measured value. Step A3 measures the loading current. Step A4 monitors the loading current. If the loading current does not change, it means that the DMFC is operating under steady loading condition. If the change of loading current exceeds a threshold value, the DMFC is operating in

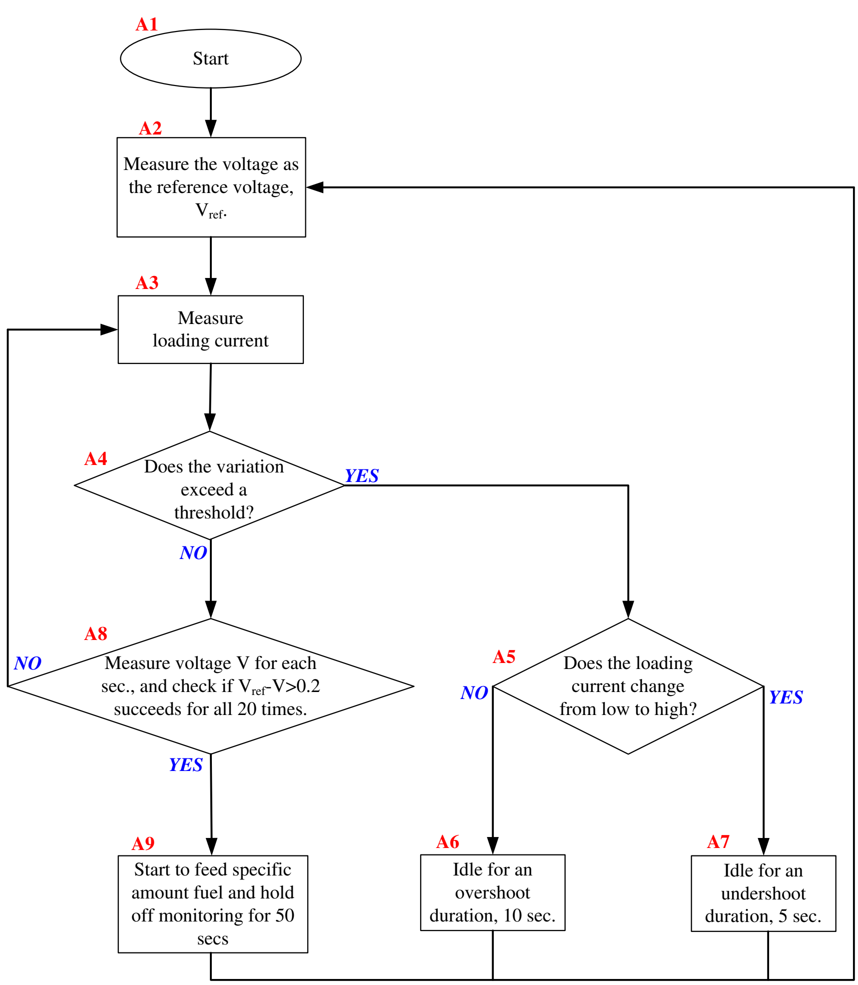

Fig. 6. The sensor-less adaptive fuel concentration control (SAFCC) algorithm.

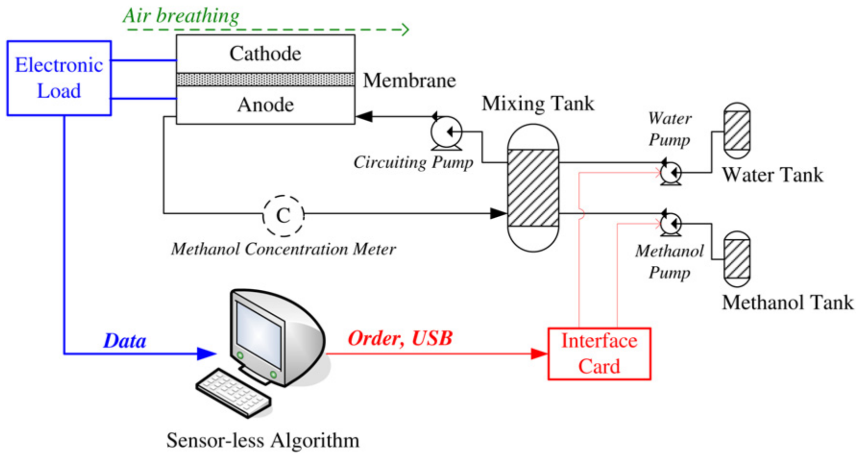

Fig. 7. DMFC testing apparatus for evaluating the SAFCC algorithm.

transient-state condition. This threshold value is to avoid misjudging the operating state due to measurement error. When the DMFC operates in transient-state, the control algorithm executes Step A5, which determines the type of transient-state. The low to high change in loading current corresponds to the undershoot phenomenon in the transient-state. On the contrary, the loading current change from high to low corresponds to the overshoot phenomenon in the transient-state. We know that transient responses take an amount of time to return back to steady-state. Hence, at Step A6 and A7, the monitoring process will be idled for a prescribed time period greater than the settling time of overshoot response or undershoot response. After that, the control algorithm goes to Step A2 to update the reference voltage. On the other hand, the control algorithm executes Step A8 when the DMFC operates in steady-state. Step A8 judges whether the actual output voltage is less than the reference value. In this case, the methanol concentration is insufficient. Then, the control mechanism will execute Step A9 to inject fuel. Step A9 feeds a specific amount of methanol into the mixing tank such that the methanol concentration will be back to the ideal range. When pure methanol has been injected into the low methanol concentration tank, time is still needed for diffusion reaction to achieve balance of methanol concentration. Hence, we hold off monitoring for 50 s at this moment. Then, the control algorithm goes to Step A2 to update the reference voltage.

In the SAFCC algorithm, the reference voltage in Step A2 is the first measured value after feeding fuel or transient-state. Hence, the reference voltage can reflect the system status automatically. The threshold values in Step A4 is to cope with misjudgment due to measurement inaccuracy. We set the threshold value according to common experience on measuring loading current. The application of this SAFCC algorithm is suitable for a large range of varying load and is independent to the DMFC status. In the constant-load operating condition, the algorithm in Fig. 6 is simplified to a flow chart by removing Steps A4–A7.

4. Experimental results and discussion

4.1. Testing apparatus for DMFCs

We set a real-time DMFC testing apparatus consisting of a DMFC module, a pure water tank, a pure methanol tank, a mixing tank, a methanol concentration meter, an electronic load, MATLAB control software, an interface card, and pumps illustrated in Fig. 7. We use air-breathing DMFC modules in this study and avoid using heater to control the temperature of cathode side. Heaters make the system complex and impractical for portable devices. The Nafion-117 based membrane electrode assembly (MEA) in the cell has an active area of $3.5 \times 3.5\ cm^2$. The anode catalyst is Pt–Ru/C and the cathode catalyst is Pt/C. A methanol concentration meter is used to measure the real-time methanol concentration. An electronic load (Type 63103, manufactured by Chroma Co, Inc., Taiwan) generates both constant and varying load. The liquid pumps are used for re-circulating the methanol solution to the cell from the mixing tank, and feeding pure methanol. All the pumps are operated with a computer via an interface card (manufactured by Syspotek Inc., Taiwan). The SAFCC algorithm is realized on the computer using Matlab/Simulink software. The optimal methanol concentration value is 4 wt%–5 wt% according to datasheet.

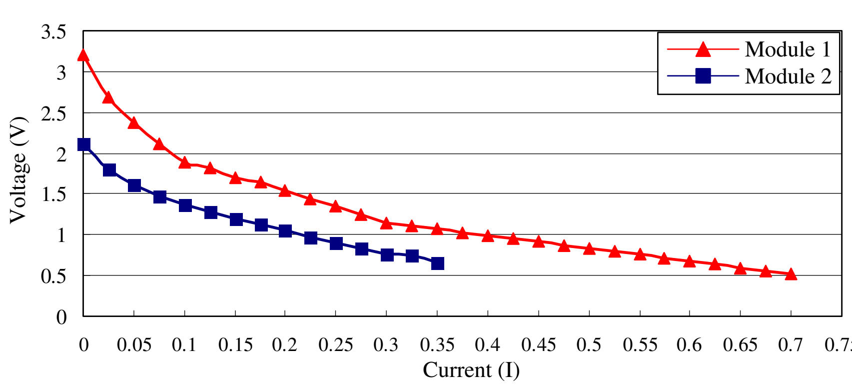

Fig. 8. Polarization curves of different modules.

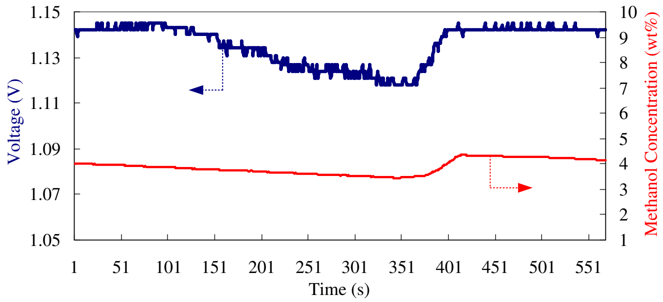

Fig. 9. The control results of Module 1 under constant load (300 mA).

4.2. Steady loading test for different modules

In order to observe the adaptability of the method, we use two different modules to test constant operating load. These two modules are the same type, but one is new and the other is used. The output behaviors vary due to operating lifetime. The performance degenerates continuously with operating lifetime. For example, the limiting current of the used module is apparently decreased. Fig. 8 shows the *I*–*V* curves of the new module (Module 1) and the used module (Module 2).

Fig. 9 shows the output voltages of Module 1, where the DMFC operates under a fixed load. In Fig. 9, the methanol concentration is sufficient till the 130th second. After that moment, the methanol concentration becomes insufficient for keeping the output voltage in a suitable level and the output voltage decreases continuously. The results after using the SAFCC algorithm are also shown in Fig. 9. At the same time, Fig. 9 also shows the decreasing output voltage due to the unsuitable methanol concentration before 365 s. The situation of too low methanol concentration is detected via the proposed algorithm. After fuel is fed to the mixing tank to increase the methanol concentration, the output voltage returns back to the stable state soon. To compare the difference of sensor-based and sensor-less approach, we consider the following scenario. We set the methanol concentration increase 0.85 wt% per each fuel injection. Typically, the suitable range of concentration lies between 4 wt% and 5 wt%. Hence, we can assume that the midpoint (4.5 wt%) is the optimal concentration value. If we use the sensor to obtain actual concentration values, the optimal injection time is when the methanol concentration value reaches down to 3.65 wt%. According to the experimental results using the sensor-less approach, as shown in Fig. 9, the injection is activated when concentration reaches down to 3.51 wt%. Therefore, a little sacrifice can achieve the sensor-less operation.

Moreover, we compare here the judging process with the method in previous literature [15–18]. They monitor the characteristic value before and after a specific period. Using this method on the experimental results in Fig. 9, with the monitoring period set to 50, 100 or 150 s, we can observe that all of these settings cannot

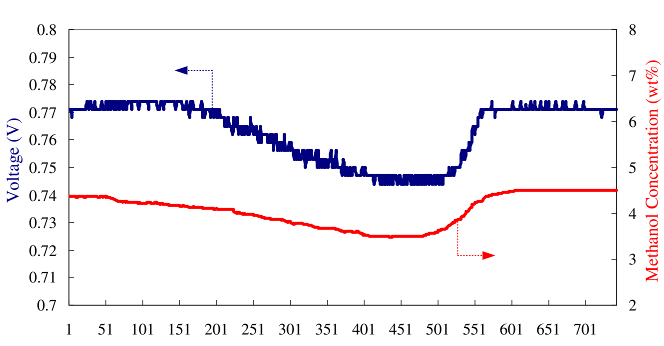

Fig. 10. The control results of Module 2 under constant load (300 mA).

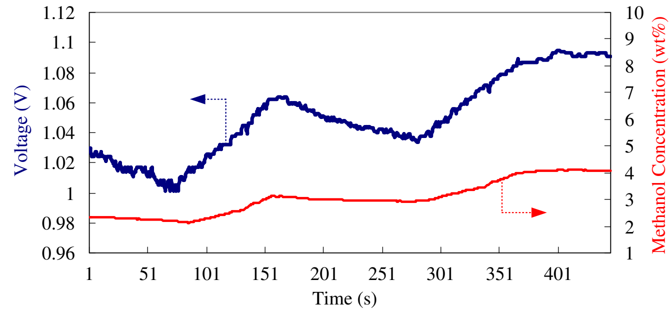

Fig. 11. The control results of Module 1 under low methanol concentration condition and constant load (350 mA).

inject fuel within 365 s. However using the SAFCC algorithm in our work, the current voltage value is always compared to the reference voltage determined in Step A2. Hence, we can achieve the fast response due to no need of monitoring periods.

The same experiment is done again by using Module 2 (a degraded DMFC), and the results are shown in Fig. 10. The control results are similar to Module 1. The output voltage and methanol concentration return back to the prescribed values soon. It proves that this approach has the adaptive capability of coping with different status of modules.

4.3. Steady loading test under low initial methanol concentration

To investigate the great capacity of the proposed algorithm, here we consider that the algorithm is initially activated under the case with low methanol concentration. Fig. 11 shows the output voltages and methanol concentration. The output voltage decrease at the beginning due to the low initial concentration. After we use this approach to control the methanol concentration, the specific amount of fuel is fed to increase the methanol concentration at the 75th second. However, the methanol concentration value is still too low after the first injection, and the output voltage decrease consistently. In this case, the control approach decides to feed fuel again at the 280th second. Finally, the methanol concentration achieves the suitable range. It shows that this approach works well even with very low initial methanol concentration.

4.4. Dynamic loading test

Fig. 12 shows the variation of output voltage when the loading current is switched from 100 mA to 300 mA. The transient response is normal before the 500th second, where the methanol concentration is sufficient. After that time, the phenomenon due to insufficient methanol concentration becomes apparent. Especially, we notice that the voltage decreases continuously when the loading current is switched to 300 mA around at the 610th second. After a little while of that moment, the methanol is injected

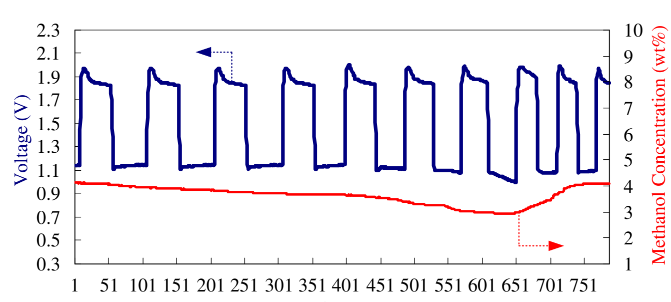

Fig. 12. The control results of Module 1 under step load (100 mA–300 mA).

automatically via running the SAFCC algorithm. Then, the output voltage returns back to the expected value and the transient response is restored to the normal type when the methanol injection is finished. We thus show the satisfactory operation performance under varying dynamic load.

5. Conclusions

An SAFCC algorithm for DMFC is proposed in this paper. The main idea comes from the observation of steady and transient behaviors caused by pulse-like change in loading current. The proposed algorithm has the merits of simple control frame, no complex mathematical equations, fast response, and adaptive capability, whereas no fuel sensors are needed. The main purpose of maintaining methanol concentration is achieved by using this algorithm. The pure methanol is injected automatically to maintain the concentration in a suitable range. In conclusion, this study has achieved the following objectives: (1) The algorithm can be used in different types of modules, and has shown its adaptive capability for both new and decayed modules; (2) The control mechanism still work well even the initial methanol concentration is very low; and (3) This method can be used under both of steady and dynamic loading conditions. It is very beneficial to maintain the prime performance of DMFC, whereas reduce the system cost and simplify system structure.

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